[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW HAMPSHIRE COLLEGE.]

SOLUBILITIES OF THE RARE EARTH SALTS OF BROMONITROBENZENESULFONIC ACID (1:4:2).

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Holmberg[1] used metanitrobenzenesulfonic acid very successfully for the separation and purification of neodymium. Derivatives of this acid, therefore, gave promise of being useful in work on the rare earths.

Bromonitrobenzenesulfonic acid (1 : 4 : 2) was prepared by the method of Limprecht.[2] The lanthanum, cerium and yttrium salts of this acid were prepared and found to be very soluble. By spontaneous evaporation yellow warty crusts finally formed, which were useless for crystallizing.

Bromonitrobenzenesulfonic acid (1 : 4 : 2) was prepared by the method of Augustin and Post.[3] In sulfonating the bromonitrobenzene it was treated at 100° with two and one-half times its weight of sulfonic acid containing 40% free sulfur trioxide, until the mixture dissolved completely in water, which required about 24 hours. The product was treated with barium carbonate and excess of soluble barium was then removed by treating with the proper amount of sulfuric acid. Considerable other acid material, besides the bromonitrobenzenesulfonic acid (1 : 4 : 2), was formed. The latter crystallized well from a boiling, saturated, aqueous solution. A pure material was obtained by a series of fractional crystallization of the crude acids. The yield was about 30%. Salts of lanthanum, cerium, yttrium and ytterbium were prepared. All crystallized nicely from solution-forming salts only very faintly tinged with the yellow color of the acid. The properties were such that this acid was seen to offer opportunity for a definit, comparative study of the properties and solubilities of a series of rare earth salts.

The compounds of the acid with yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, erbium, thulium, and ytterbium were prepared and crystallized from solution. The first crop of crystals only was used in this work.

The composition was found by determination of water of crystallization, by heating the air-dry crystals to 200°, and by determination of R_2O_3 by means of the oxalate precipitation and ignition. In the case of praseodymium the oxalate was titrated with a standard potassium permanganate solution. Results are as follows:

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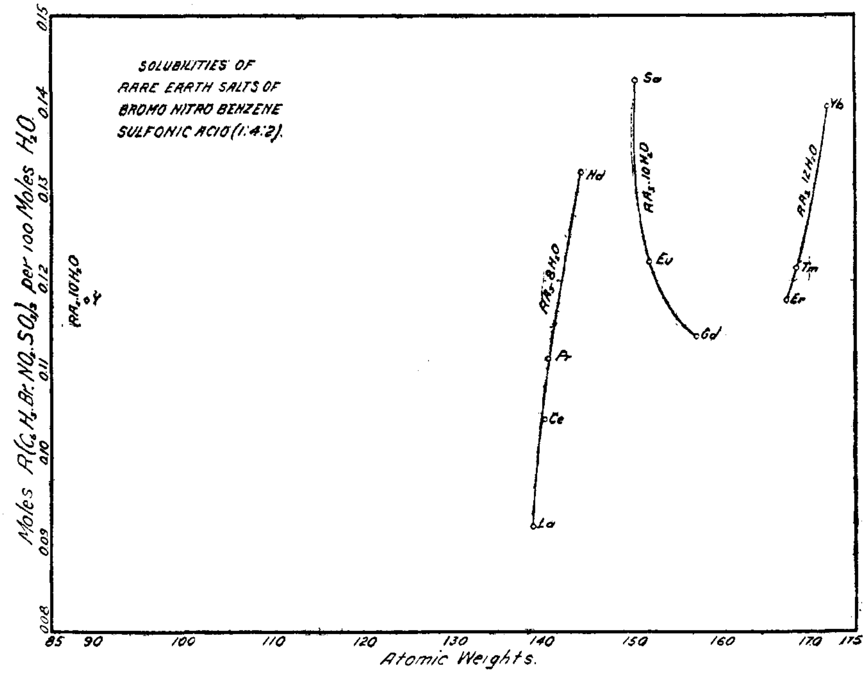
[1] *Chem. Centr.*, 1906, II, 1695.

[2] *Ber.*, 8, 456.

[3] *Ibid.*, 8, 1559.

	H_2O.		R_2O_3.	
	Calculated. Per cent.	Found. Per cent.	Calculated. Per cent.	Found. Per cent.
$Y(C_6H_3\overset{1}{Br}.\overset{4}{NO_2}.\overset{2}{SO_3})_3.10H_2O$	16.29	15.90	10.16	10.13
	...	15.98	...	10.07
$La(C_6H_3\overset{1}{Br}.\overset{4}{NO_2}.\overset{2}{SO_3})_3.8H_2O$	12.80	12.80	14.46	14.41
	...	12.90	...	14.38
$Ce(C_6H_3\overset{1}{Br}.\overset{4}{NO_2}.\overset{2}{SO_3})_3.8H_2O$	12.78	12.60	14.58	14.50
	...	12.60	...	14.58
$Pr(C_6H_3\overset{1}{Br}.\overset{4}{NO_2}.\overset{2}{SO_3})_3.8H_2O$	12.78	13.05	14.59	14.40
	...	12.78	...	14.43
$Nd(C_6H_3\overset{1}{Br}.\overset{4}{NO_2}.\overset{2}{SO_3})_3.8H_2O$	12.74	12.82	14.88	14.79
	...	12.66	...	14.82
$Sa(C_6H_3\overset{1}{Br}.\overset{4}{NO_2}.\overset{2}{SO_3})_3.10H_2O$	15.35	15.01	14.86	14.90
	...	14.96	...	14.90
$Eu(C_6H_3\overset{1}{Br}.\overset{4}{NO_2}.\overset{2}{SO_3})_3.10H_2O$	15.34	14.98	14.91	14.83
	...	15.33	...	14.98
$Gd(C_6H_3\overset{1}{Br}.\overset{4}{NO_2}.\overset{2}{SO_3})_3.10H_2O$	15.27	14.93	15.36	15.43
	...	14.99	...	15.47
$Er(C_6H_3\overset{1}{Br}.\overset{4}{NO_2}.\overset{2}{SO_3})_3.12H_2O$	...	...	15.60	15.62
	...	...	...	15.62
$Tm(C_6H_3\overset{1}{Br}.\overset{4}{NO_2}.\overset{2}{SO_3})_3.12H_2O$	...	...	15.68	15.64
	...	...	...	15.43
$Yb(C_6H_3\overset{1}{Br}.\overset{4}{NO_2}.\overset{2}{SO_3})_3.12H_2O$	...	...	15.96	15.95
	...	...	...	16.02



In the case of the erbium, thulium and ytterbium compounds, which contained twelve molecules of water of crystallization, the water could not be determined, because at the temperature used for the other salts, these were charred, while at a lower temperature, the water was not all evolved.

The colors of the salts of praseodymium, neodymium, samarium, erbium and thulium were not modified noticeably by the color of the acid radical. The compounds containing eight molecules of water of crystallization formed needle-like crystals; those containing ten molecules, thin orthorhombic plates, and those containing twelve molecules less regular plates and needles.

The solubilities were determined after allowing equilibrium to become adjusted by rotation in a thermostat kept constant at 25°. The following results are averages of duplicates:

	Moles anhydrous salt per 100 moles H_2O.	Per cent. anhydrous salt.
$Y(C_6H_3\overset{1}{Br}.\overset{4}{N}O_2.\overset{2}{S}O_3)_3$	0.1178	5.739
$La(C_6H_3\overset{1}{Br}.\overset{4}{N}O_2.\overset{2}{S}O_3)_3$	0.09207	4.771
$Ce(C_6H_3\overset{1}{Br}.\overset{4}{N}O_2.\overset{2}{S}O_3)_3$	0.1043	5.559
$Pr(C_6H_3\overset{1}{Br}.\overset{4}{N}O_2.\overset{2}{S}O_3)_3$	0.1112	5.730
$Nd(C_6H_3\overset{1}{Br}.\overset{4}{N}O_2.\overset{2}{S}O_3)_3$	0.1322	6.762
$Sa(C_6H_3\overset{1}{Br}.\overset{4}{N}O_2.\overset{2}{S}O_3)_3$	0.1427	7.272
$Eu(C_6H_3\overset{1}{Br}.\overset{4}{N}O_2.\overset{2}{S}O_3)_3$	0.1222	6.310
$Gd(C_6H_3\overset{1}{Br}.\overset{4}{N}O_2.\overset{2}{S}O_3)_3$	0.1137	5.938
$Er(C_6H_3\overset{1}{Br}.\overset{4}{N}O_2.\overset{2}{S}O_3)_3$	0.1178	6.056
$Tm(C_6H_3.\overset{1}{Br}.\overset{4}{N}O_2.\overset{2}{S}O_3)_3$	0.1214	6.379
$Yb(C_6H_3\overset{1}{Br}.\overset{4}{N}O_2.\overset{2}{S}O_3)_3$	0.1397	7.294

The solubilities plotted against atomic weights are shown graphically in the accompanying diagram. It is seen that, with change in the water of hydration, there is a change in direction of the solubility curve, which amounts to a reversal of the slope. The phenomenon shown may be compared to that producing the change in the general direction of the temperature-solubility curve of a single salt forming various molecular compounds with water at different temperatures. That is, with a break in the general direction of the solubility curve, there is a change in the nature of the compound.

Work on the separation of various rare earths by crystallizing salts of bromonitrobenzenesulfonic acid (1 : 4 : 2) is now under way in this laboratory.

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